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Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Area 43 MWR Gas Station Marine Corp Base, Camp Pendleton, California

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Submitted to the U.S. Navy, Southwest Division
Naval Facilities Engineering Command, San Diego, California

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1. Program Overview

1.1. Introduction

In June 1994, the State Water Resource Control Board (SWRCB) contracted with the Lawrence Livermore National Laboratory/University of California (LLNL/UC) Leaking Underground Fuel Tank (LUFT) Team to study the cleanup of LUFTs in California. The study consisted of data collection and analysis from LUFT cases and a review of other studies on LUFT cleanups. Two final reports were submitted to the SWRCB in October and November 1995. These reports were entitled: *Recommendations To Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)* (Rice et al., 1995a); and *California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis* (Rice et al., 1995b).

1.2. LUFT Demonstration Cleanup Program

1.2.1. Background

One of the important recommendations of this study was to identify a series of LUFT demonstration sites and to form a panel of experts made up of scientific professionals from universities, private industry, and Federal and State regulatory agencies. This panel would provide professional interpretations and recommendations regarding LUFT evaluations and closures at demonstration sites.

As a result of this recommendation, ten Department of Defense (DOD) sites were selected. Site selection was coordinated through the California Military Environmental Coordination Committee (CMECC) Water Process Action Team (PAT). Sites were selected to represent each branch of the military services with bases in California, as well as a number of Regional Water Quality Control Boards (RWQCB) and the diverse hydrogeologic settings in California where fuel hydrocarbon contaminant (FHC) cleanup problems occur. The Camp Pendleton Marine Corps Base, Area 43 gas station, within the San Diego RWQCB, is one of the sites selected to participate in the DOD Petroleum Hydrocarbon Cleanup Demonstration (PHCD) Program. This program will be referred to as the DOD LUFT Demonstration Cleanup Program.

The other sites selected and their corresponding RWQCB region are:

- Army Presidio at San Francisco, San Francisco RWQCB.
- Barstow Marine Corps Logistic Center, Lahontan RWQCB.
- Castle Air Force Base, Central Valley RWQCB.
- China Lake Naval Weapons Center, Lahontan RWQCB.
- El Toro Marine Corps Air Station, Santa Ana RWQCB.
- George Air Force Base, Lahontan RWQCB.
- Port Hueneme Naval Construction Battalion Center, Los Angeles RWQCB.
- Travis Air Force Base, San Francisco RWQCB.
- Vandenberg Air Force Base, Central Coast RWQCB.

The Expert Committee (EC) selected to evaluate the selected demonstration sites are:

- Mr. David W. Rice, LLNL, Environmental Scientist; Project Director SWRCB LUFT Re-evaluation Project; LLNL/UC LUFT Team member; DOD FHC Demonstration Program Coordinator.
- Dr. Walt McNab, LLNL, Hydrogeochemist, with expertise in the evaluation of passive bioremediation processes.
- Dr. William E. Kastenbergh, UC, Berkeley, Professor and Chairman, Department of Nuclear Engineering; member of LLNL/UC LUFT Team, with expertise in environmental decision making and decision analysis processes.
- Dr. Lorne Everett, UC, Santa Barbara, Hydrogeologist; head of the Vadose Zone Research Laboratory and member of LLNL/UC LUFT Team, with expertise in vadose zone FHC transport mechanisms and passive bioremediation processes.
- Dr. Stephen Cullen, UC, Santa Barbara, Hydrogeologist; member of LLNL/UC LUFT Team with expertise in vadose zone FHC transport mechanisms and passive bioremediation processes.
- Dr. Paul Johnson, Arizona State University, Chemical Engineer; primary author of *American Society for Testing and Materials (ASTM) RBCA* guidance, with expertise in chemical fate and transport.
- Dr. Michael Kavanaugh, former Chairman, National Research Council Alternatives for Groundwater Cleanup Committee; Vice President, Malcolm Pirnie, Inc., with expertise in evaluation of groundwater remediation alternatives and environmental decision making processes.
- Mr. Matthew Small, U.S. EPA Region IX, Hydrogeologist; Co-Chairman of U.S. EPA Remediation by Natural Attenuation Committee, with expertise in risk-based corrective action and passive bioremediation.

1.2.2. Risk-Based Corrective Action

The LLNL/UC recommendations report concluded that risk-based corrective action (RBCA) provides a framework to link cleanup decisions to risk. The DOD LUFT Demonstration Cleanup Program provides a series of sites where the application of a risk-based cleanup approach can be demonstrated.

For a risk to exist, there must be a source of a hazard, a receptor, and a pathway that connects the two. All three factors must be addressed to determine whether a LUFT release poses a risk to human health, safety, or the environment. If the source, pathway, or receptor are at all times absent, there is, by definition, no risk. The distinction between sources, pathways, and receptors may be context-dependent in many cases and therefore must be carefully defined. For purposes of the present assessment, definitions of these terms are developed by working backward from the receptor to the source:

Receptor: Human or ecological risk receptors which may potentially be subject to damage by exposure to hydrocarbons via ingestion, inhalation, or absorption. This definition also specifically includes water-supply wells because it must be assumed that humans will be ingesting the water from these wells.

Pathways: Physical migration routes of contaminants from sources to risk receptors. This definition specifically includes the groundwater environment downgradient of the source which provides a medium through which dissolved contaminants may migrate to water-supply wells, as well as to surface water bodies which may serve as ecological risk pathways. The definition also includes the vadose zone in the immediate vicinity of the source, where vapor migration routes to nearby human receptors may exist.

Sources: Points of entry of contaminants into possible exposure pathways. In the case of hydrocarbon releases associated with LUFT sites, separate-phase hydrocarbon product which can either dissolve into the aqueous phase or volatilize into the gaseous phase constitutes a source. Primary sources will include underground tanks and associated piping; secondary sources will include any separate-phase hydrocarbon or free product material residing within sediment pores.

From a mathematical viewpoint, sources and receptors represent boundary conditions for the problem of interest (influx and outflux, respectively); pathways represent the problem domain. Thus, in some special situations, the dissolved plume in groundwater may represent a source, such as in the case of Henry's law partitioning of contaminants from the aqueous phase into the gaseous phase. On the other hand, hydrocarbons which have adsorbed onto sediment surfaces from the aqueous phase cannot be regarded as potential sources in most situations according to this definition, but rather exist as part of the pathway.

Risk characterization is defined as an information synthesis and summary about a potentially hazardous situation that addresses the needs and interests of decision makers and of interested and affected parties. Risk characterization is a prelude to cleanup decision making and depends on an iterative, analytic, and deliberative process. This process attempts to gather all relevant data so the decision makers may then choose the best risk-management approach.

1.2.3. The Appropriate Use of Passive Bioremediation

The Recommendations Report also concluded that with rare exceptions, petroleum fuel releases will naturally degrade (passively bioremediate) in California's subsurface environments. The DOD LUFT Demonstration Cleanup Program provides sites where the appropriate use of passive bioremediation can be evaluated.

Passive bioremediation can control groundwater contamination in two distinct ways:

- First, passive bioremediation substantially lowers the risk posed to downgradient risk receptors through plume stabilization¹.
- Second, passive bioremediation actively destroys fuel hydrocarbon mass in the subsurface, leading to remediation of contamination over time (e.g., eventual contaminant concentration decline and depletion of the dissolved hydrocarbon plume). From a risk management viewpoint, the stabilization of the dissolved plume and associated reduction in exposure potential is the most important contribution of passive bioremediation.

The role of passive bioremediation in controlling the behavior of dissolved hydrocarbon plumes may be evaluated through both primary and secondary field evidence.

- Primary evidence includes quantitative evaluation of plume stability or plume shrinkage based upon trends in historical groundwater contaminant concentration data.
- Secondary evidence includes indirect indicators of passive bioremediation, such as variations in key geochemical parameters (dissolved oxygen, nitrate, sulfate, iron, manganese, methane, alkalinity/carbon dioxide, Eh, pH) between measurements in fuel hydrocarbon-impacted areas and background.

Although primary evidence of plume stability or decline generally provides the strongest arguments to support natural attenuation at a given site, such evidence may not be available because adequate historical groundwater monitoring may not exist. In these cases, short-term monitoring data providing secondary lines of evidence, in conjunction with modeling where

¹ Even in the presence of a continuous constant source of fuel hydrocarbons (e.g., dissolution of residual free product components trapped in the soil matrix), a groundwater plume subject to passive bioremediation will reach a steady-state condition in which plume length becomes stable. This will occur when the rate of hydrocarbon influx from dissolution of the residual free product source is balanced by the rate of mass loss via passive bioremediation, integrated across the entire spatial extent of the plume.

appropriate, may support a hypothesis for the occurrence of passive bioremediation. Consequently, means for assessing the role of passive bioremediation in controlling risk by secondary lines of evidence should be fully explored at such sites.

Appropriate use of passive bioremediation as a remedial alternative requires the same care and professional judgment as the use of any other remedial alternative. This includes site characterization, assessment of potential risks, comparison with other remedial alternatives, evaluation of cost effectiveness, and the potential for bioremediation to reach remedial goals. Monitoring process and contingency planning must be considered as well.

Passive bioremediation may be implemented at a given petroleum release site either as a stand-alone remedial action or in combination with other remedial actions. The need for active source removal must also be addressed on a site-by-site basis. Source removal includes removing leaking tanks and associated pipelines, and any remaining free product and petroleum fuel saturated soil, as much as economically and technically feasible. When properly used, passive bioremediation can help manage risk and achieve remedial goals.

1.2.4. The DOD LUFT Demonstration Cleanup Program Steps

The demonstration program process can be summarized in the following nine steps:

- Step 1: Site scoping meeting with site staff, regulators, and EC staff representatives. Develop and discuss site conceptual model. Identify and discuss pathways and receptors of concern.
- Step 2: RBCA training for DOD Petroleum Hydrocarbon Cleanup Demonstration Program (PHCDP) participants.
- Step 3: Site staff and contractors prepare the data package. EC staff reviews available data and identifies data gaps needed to apply a risk-based cleanup approach.
- Step 4: EC visits site and receives briefing, on site characterization, conceptual model, and pathways and receptors of concern. Site tour is included in this briefing. Following EC's visit, a site characterization report is prepared by the EC containing recommendations for further data collection, if needed (See Appendix A).
- Step 5: EC staff applies a risk based cleanup approach to the site using best available data.
- Step 6: EC staff evaluates the natural attenuation potential for the site using best available data. An estimate of the time to clean up and the uncertainty associated with this estimate will be made. Sampling and monitoring procedures to support intrinsic bioremediation for the site will be identified.
- Step 7: Based on the concept of applied source, pathways, and receptors as to potential hazards, site specific findings regarding natural attenuation potential, and discussion with regulators, the EC shall provide its recommendations for an appropriate risk-management strategy at the site and the set of actions needed to achieve site closure. The EC will present its recommendations at an appropriate forum.
- Step 8: The EC will provide a DOD LUFT Demonstration Cleanup Program overall evaluation comparing the effectiveness of risk based cleanup at each site in the program. An estimation of the cost savings using risk based cleanup protocols will be compared to baseline approaches. An estimation of the value of the remediated water will be made.

- Step 9: The EC Staff will produce a DOD Risk Execution Strategy for Clean-Up of the Environment (RESCUE) implementation guide and accompanying procedures manual (Phase I, Petroleum) that can be used in California and in other states by military bases.

2. Site Overview

2.1. Background

The Area 43 Morale, Welfare, and Recreation (MWR) Gas Station is located in the Las Flores groundwater basin at the Marine Corps Base (MCB), Camp Pendleton. The gas station was constructed in 1958 and is currently in operation as an automobile filling station. The site is bounded by undeveloped land to the north and south, Las Flores Creek to the east, and Las Pulgas Road to the west.

Two previous 10,000-gallon gasoline underground storage tanks (USTs) and a 550-gallon waste oil tank were removed from the site in October 1993. An initial site assessment was conducted by IT Corporation following tank removal and included the advancement of nine boreholes and the installation of three groundwater monitoring wells. This investigation indicated that FHCs, including benzene, toluene, ethylbenzene, and xylenes (BTEX), had impacted both soil and groundwater at the site. Additional soil and groundwater investigations were conducted by OHM Remediation Services between 1995 through 1997. These investigations, which have included additional soil borings, monitoring wells, and Hydropunch sampling, have further delineated the extent of the soil and groundwater contamination. The release history and the total volume of FHCs released to the subsurface are generally unknown. The impact of the FHCs on the nearby Las Flores Creek, downgradient of the release area, has not been definitively established.

2.2. Site Conceptual Model

2.2.1. Geology and Hydrogeology

Sediments underlying the Area 43 MWR Gas Station consist of unconsolidated fill (sand, clayey silt) and alluvium (interbedded sands, silts, and clays) across the depth range spanned by exploratory boreholes (approximately 26.5 feet). Fill material generally occupies the uppermost 5 to 15 feet of the geologic section. The asphalt/concrete cover over much of the site is likely to preclude significant vertical recharge from infiltration.

At least two distinct hydrostratigraphic units appear to exist underneath the site. The upper unit, apparently unconfined, spans the base of the fill to a clay bed, approximately four feet thick, which may act as a confining unit on the underlying deeper zone. Differences in water levels between the two zones in two well pairs (MW-01 and MW-01A, MW-05A and MW-05B) suggest that the hydraulic head in the lower zone may be one to three feet higher than in the upper zone. Average depth to groundwater at the site is approximately 15 feet, with observed seasonal fluctuations in groundwater elevation on the order of two feet. Estimated transmissivity values reported for the Area 43 MWR Gas Station range from approximately 800 to 900 gallons day⁻¹ ft⁻¹ based on pumping test data analyzed from three observation wells by the Theis and Cooper-Jacob methods (OHM, 1997). Assuming a mean aquifer thickness of 5 to 10 feet (based on interpretive geologic cross sections), the corresponding hydraulic conductivity estimates range from 80 to 180 gallons day⁻¹ ft⁻² (1 to 2.2 ft/day). Taking into consideration the reported

mean hydraulic gradient of 0.08 ft/ft and assuming a porosity on the order of 0.30, the groundwater pore velocity under the site should be on the order of approximately 0.3 to 0.6 ft/day. Groundwater flow direction is toward the southeast.

The site is located in the Las Flores groundwater basin, with surface drainage generally directed toward the west-southwest. The site lies approximately 100 feet to the north of the Las Flores Creek. Given the depth to groundwater at the site and the apparent elevation of the creek relative to the gas station, it is possible that the creek acts as an effluent stream (i.e., gaining water from subsurface discharge). However, the hydrostratigraphic relationship between the upper water-bearing zone and the creek remains unclear; it is possible that the FHC-impacted aquifer may pass underneath the creek bed.

2.2.2. Distribution of Contaminants

The current extent of FHC soil and groundwater contamination has been delineated by 13 soil borings, eight groundwater monitoring wells, and eight Hydropunch samples. Soil contamination (TPH as gasoline, BTEX constituents) has been observed in 8 soil borings, with concentrations of TPH-G ranging up to 5,300 mg/Kg (at a depth of 8 ft in B-2 as well as at 15 ft in B-9 - above water table). While much of the soil contamination appears to be associated with the former tank locations, the FHC detections in B-1 and B-2 near the pump island location suggest that releases occurred from the piping system as well. The observed increases in soil concentrations of TPH-G and BTEX components with depth in several borings, with the highest concentrations immediately overlying the water table at 15 feet, may be explained by a fluctuating groundwater table or a previous layer of floating free product. Synthetic precipitation leaching procedure (SPLP) tests have been conducted on site sediment samples in an attempt to quantify the potential for residual entrapped hydrocarbons to impact groundwater. The maximum release concentration suggested by this analysis was 1,050 mg/L for benzene in a soil sample containing 4.89 mg/Kg benzene and 900 mg/Kg TPH-G (B-11 at a depth of approximately 15 ft). However, SPLP analyses showed little or no leachable FHCs in soil samples collected from equivalent depths in MW-01A, B-13, HP-1, HP-2 (7 ppb benzene at 14 ft), HP-3, HP-4, HP-5, and HP-7. Because of the highly localized nature of residual FHC sources implied by the SPLP analyses, the extent of the impact of leaching is very unclear because of expected spatial and temporal variability in the groundwater and soil water fluid flow field.

FHCs have been historically detected in groundwater on a consistent basis only in monitoring wells MW-03 and MW-04. FHCs have also been detected in one round of sampling in the recently installed wells MW-01A, MW-05A, and MW-06. The highest FHC concentrations noted in site monitoring wells include 48 mg/L TPH-G and 3.1 mg/L benzene in MW-01 in September 1995. Concentrations in this well have fallen to below detection limits in recent sampling events. Currently, the highest FHC concentrations are observed in MW-04 (25 mg/L TPH-G and 1.1 mg/L benzene). Groundwater samples obtained as part of a Hydropunch survey conducted in March 1997, revealed that five out of a total of eight samples contained detectable concentrations of FHCs, with the highest concentrations in HP-2 at 85 mg/L TPH-G and 1.6 mg/L benzene. Free product has not been historically observed in site monitoring wells to date. Interpreted concentration contours for total BTEX concentrations in groundwater in March–April 1997, are shown on Figure 1.

The fuel-oxygenate methyl tertiary butyl ether (MTBE) has been detected in site groundwater in association with the FHCs (MW-01, MW-01A, MW-02, MW-04, MW-05A, HP-2, HP-3, HP-4, HP-5, and HP-7). Interpreted concentration contours for MTBE concentrations in groundwater in March–April 1997, are shown on Figure 2. The highest concentration detected to date has been approximately 2.8 mg/L in MW-05A in April 1997. Unlike FHCs, MTBE is known to be currently present in the deeper water-bearing zone in one well (MW-01).

Additional sediment and surface water samples were collected in 1997 to assess FHC impact to the Las Flores Creek. FHCs were detected in a hand-augered soil sample collected on the northwest creek bank adjacent to the service station at a depth of 14 ft (160 mg/L TPH-G and 0.430 mg/L benzene). However, no FHCs were detected in either surface water samples collected from the creek or in sediment samples collected from the creek bed area.

3. Risk Analyses and Management

3.1. Sources

3.1.1. Primary Source(s)

Primary sources of FHC contamination are defined as engineered structures such as underground tanks, pipelines, and sumps which leak and release product into the subsurface environment. Primary sources at the Area 43 MWR Gas Station include the previous two 10,000-gallon gasoline storage tanks and a 550-gallon waste oil tank, all of which were removed in October 1993. The underground piping system was also replaced during tank removal. The extent of soil over-excavation associated with tank removal activities is unknown.

3.1.2. Secondary Source(s)

Secondary contamination sources include residual free product which could remain in unsaturated soils as well as on top of the water table even after primary sources have been removed. Free product has not been observed in site monitoring wells to date. Analyses of soil samples, including synthetic precipitation leaching procedure (SPLP) testing, have suggested that relatively low concentrations of FHC or BTEX currently reside in the vadose zone. Most detections have been noted near the water table, where groundwater level fluctuations have probably acted to smear the contaminant profile about the vadose zone-saturated zone interface.

3.2. Receptors

3.2.1. Present and Anticipated Future Human Health Receptors

The nearest known existing water-supply wells are approximately four miles downgradient from the Area 43 MWR Gas Station. Because the release site and associated groundwater plume are entirely within the MCB property boundary, it is expected that institutional controls will continue to be in place to assure that future water-supply wells are not installed in the vicinity where they would be at risk. Residential barracks exists across Las Pulgas Road, which may constitute theoretical FHC vapor receptors.

3.2.2. Ecological Risk Receptors

The Las Flores Creek and associated ecosystem, approximately 100 feet downgradient from the former tank area, constitutes an ecological receptor potentially at risk to FHC impact (from aquifer discharge as well as vapor migration) from the site. The creek area includes the habitat of the endangered Least Bell's vireo. See Appendix B for a discussion regarding the assessment of ecological impacts.

3.3. Exposure Pathways

To pose a human health or ecological risk, the source of contaminants (e.g., residual free product) must be linked to receptors (e.g., water-supply wells) via pathways. At the Area 43 MWR Gas Station, the groundwater pathway between the former tank area and the Las Flores Creek constitutes a possible exposure pathway. The pathway between the service station and the residential barracks across Las Pulgas Road presents an additional theoretical vapor transport pathway.

3.3.1. Factors Influencing Groundwater Hydrocarbon Plume

Probability distribution functions of benzene plume lengths reported in the LUFT Historical Case Analysis (Rice et al., 1995) included a median (50th percentile) value of approximately 100 feet and a 90th percentile value of approximately 260 feet. Many plumes evaluated by the LUFT Historical Case Analysis appeared to have stabilized into an apparent steady state condition. This stability is likely a reflection of the interplay between transport processes and passive bioremediation, where the input of dissolved FHCs from residual sources is balanced by FHC losses integrated across the spatial extent of the plume.

In the instance of the Area 43 MWR Gas Station, the proximity of the Las Flores Creek to the FHC source (approximately 100 feet) implies that risk of FHC impact to the creek may be significant. Therefore, contaminant fluxes should be quantified, and natural attenuation processes taken into account to evaluate the potential impact to the Las Flores Creek ecology.

3.3.1.1. Passive Bioremediation

Groundwater quality data are being collected to support a possible remediation-by-natural-attenuation alternative, as suggested by the San Diego Regional Water Quality Control Board (SDRWQCB) in a letter to the MCB dated June 19, 1996. However, given the relatively brief groundwater monitoring period and the small number of monitoring points associated with the Area 43 MWR Gas Station, direct primary evidence of passive bioremediation is not available. Because of the apparent interaction of the plume with the creek bed area, and the potential damage to the creek bed that extensive plume delineation sampling may cause, an objective measure of plume length is also unavailable for analysis. Nevertheless, secondary evidence of FHC passive bioremediation in the form of geochemical indicator parameters is available. Dissolved oxygen, nitrate, sulfate, iron, methane, alkalinity, pH, and redox potential (E_h) were measured in a number of groundwater samples collected from monitoring wells and a Hydropunch survey in March and April 1997. Statistical analyses of these data are strongly suggestive that a number of passive bioremediation processes are active in groundwater at the site, particularly sulfate reduction, iron reduction, and methanogenesis. These findings pertain to BTEX only and not to MTBE. To date, conclusive field evidence of MTBE biodegradation or abiotic transformation has not been reported in the literature.

Analyses of passive bioremediation signatures in groundwater are discussed in Appendix C. Soil gas survey results presented by OHM (1997) are consistent with the hypothesis that some degree of FHC passive bioremediation is occurring with unsaturated soils as well, with elevated concentrations of carbon dioxide and depleted levels of oxygen in soil gas. Whether these findings reflect FHC biodegradation or microbial activity associated with other substrates is unclear.

3.3.1.2. Plume Migration and Impact to Stream

Based on pumping test results and the interpreted local hydraulic gradient, groundwater pore velocities at the Area 43 MWR Gas Station are on the order of 0.3 to 0.6 ft/day. At this rate,

groundwater can migrate from the former tank area to the Las Flores Creek, some 100 feet downgradient, in approximately 170 to 380 days (neglecting the effects of retardation).

Mean first-order degradation rates have been reported for BTEX plumes in the field by a number of workers (e.g., MacIntyre et al., 1993; Wilson et al., 1995; Buscheck et al., 1996; Chapelle et al., 1996). A degradation rate of $0.8\% \text{ day}^{-1}$, a typical, if not high, value for anaerobic conditions, corresponds to a half-life of approximately 87 days. Thus, during migration from the source area to the Las Flores Creek, dissolved hydrocarbons could be expected to degrade through some 2 to 4 half-lives, corresponding to a reduction in concentration of 74% to 95%. Given the benzene concentrations ranging between 1 to 3 mg/L encountered in MW-04 and HP-4, this implies that the plume could still be characterized by benzene concentrations on the order of 0.50 to 0.790 mg/L in the vicinity of the creek (neglecting retardation as well as dispersive effects). Given this range of concentrations, the estimated groundwater velocity, mean aquifer thickness and an assumed contact length between the plume and the creek bank of approximately 100 feet, these estimates would imply a mass discharge of benzene into (or under) the Las Flores Creek of approximately 100 to 2,000 mg/day. A greater potential for MTBE to enter the creek exists because MTBE does not undergo passive bioremediation to the vigorous extent observed with respect to FHCs.

Despite the potential for FHCs and MTBE to enter the creek bed, analyses of surface water and creek sediment samples collected in the area of the service station failed to indicate detectable levels of these contaminants. Several explanations may account for this observation:

- The FHC/MTBE plume passes underneath the creek bed, rather than the contaminated water-bearing zone discharging directly into the creek;
- Volatilization and dispersion processes rapidly dilute the contaminants below applicable detection limits;
- Because of the dynamic, transient nature of flow and transport process in the creek, samples collected during the single sampling event simply missed locations where contaminants might have been present.

An additional round of sampling in the creek bed, both of surface water and sediments, is warranted to confirm the preliminary findings. These samples should be collected some distance downgradient to provide a greater chance of detecting FHCs if they are indeed present. However, care must be taken not to damage the creek ecosystem as a result of sampling activities (i.e., use of heavy equipment should be avoided).

3.3.1.3. Vertical Migration of Contaminants

Vertical migration of contaminants from the upper water-bearing zone into the lower constitutes an additional groundwater migration pathway. However, the existence of a clay layer between these two zones and an apparent hydraulic head difference which would oppose downward migration suggests that this is probably not a major pathway. Currently, FHCs are not found in groundwater samples collected from the two wells screened in the deeper zone, MW-01 and MW-05B, although significant concentrations of TPH-G and BTEX were noted in MW-01 in 1995 and a trace level of TPH-G detected in October 1996. MTBE has been detected in low levels in MW-01 which appear to be declining (0.097 mg/L in July 1996, 0.064 mg/L in October 1996, 0.048 mg/L in February 1997, and 0.047 mg/L in April 1997).

3.3.2. Hydrocarbon Vapor Migration

Given the relatively low concentrations of FHCs found in soil and groundwater at the Area 43 MWR Gas Station and the absence of free product in site monitoring wells, the risk posed by migration of hydrocarbon vapors from the release to nearby receptors is probably very low. The

residential barracks is too far away from the source area (greater than 100 feet) to be affected by FHC vapors. The risk posed to the service station workers by exposure to vapors from the release is very small in comparison to everyday workplace exposure levels encountered at gas stations and similar facilities. While there is some risk to human health associated with FHC vapors, such risks fall under the jurisdiction of occupational health and safety laws; the added risk from subsurface FHCs released to soils and groundwater is probability insignificant.

3.4. Remedial Goals

Cleanup requirements or standards are set by states to ensure that sufficient contamination is removed to protect human health and the environment. Under this broad umbrella of concerns, state-specific considerations such as groundwater use, aquifer beneficial use designation, cleanup costs versus risks, technical feasibility of cleanup, available expertise, available funding, permitting, land use, and property transfers may also play a role in setting these standards.

The cleanup standards set by states usually fall into one of three broad categories:

1. Technology based standards, which are based on the detection limits of analytical laboratory equipment.
2. Subjective standards, which are often adopted based on technology limits or in the absence of another mechanism; these standards may require cleanup to non-detectable or background levels.
3. Risk-based standards, which can be either an overall standard based on conservative yet realistic exposure and toxicity analysis, or site-specific standards based on site-specific conditions, land use, and exposure scenarios.

To establish remedial goals, these standards are then applied either at all locations throughout the plume or at some boundary beyond which the plume cannot be allowed to migrate. Remedial goals may also include some time frame within which the goals must be met. If conditions at the site do not exceed remedial goals, the site will usually receive a status of "no further action required at this time." However, if site conditions do exceed remedial goals, then several choices exist (Small, 1993):

- Cleanup to background or non-detect: This approach is very protective of human health and the environment, but can often prove to be prohibitively expensive or technically infeasible.
- Cleanup to an overall or generic standard: This approach is also protective, feasible in many cases, and generally less expensive than cleanup to background or non-detect levels. However, these levels may still prove to be prohibitively expensive, or even technically infeasible for some sites.
- Cleanup to a site-specific standard: The protectiveness of this approach is usually based on specified land uses and may need to be re-evaluated if changes occur. The cleanup levels are often more feasible and generally less expensive to achieve. However, this approach requires potentially expensive site-specific exposure and risk assessment, to determine threats and impacts.
- Risk management, or containment: When contaminant concentrations exceed safe levels, but cannot feasibly be cleaned up, or there are no current or future exposure pathways, then risk management through containment of contamination to prevent further migration

may be an option. Active containment systems are often expensive to install and maintain.

- **No Action:** In some instances monitoring may not be needed or may eventually be discontinued. As with monitored natural attenuation, this approach may require site-specific exposure and risk assessment, to determine threats and impacts to public health and the environment.

At Area 43 MWR Gas Station site, the potential impact of the FHC plume (or active efforts to remediate the plume) on the local aquatic ecosystem must be taken into account.

3.4.1. Remedial Technology or Process Selection

If contaminant concentrations exceed remedial goals and cleanup is required, then a cleanup technology must be selected based on the information obtained from site assessment and characterization. This technology should be selected based on the ability to meet remedial goals, site conditions, and physio-chemical properties of the contaminants. The technology should not create additional hazards (e.g., air sparging without soil vapor extraction that may potentially transport vapors into buildings).

The technology should ideally perform this task as quickly, efficiently, and cost-effectively as possible. It is also important to give some consideration to how the cleanup technology or process actually accomplishes concentration reductions and where the removed contaminants or by products are actually going. There are four basic alternatives:

1. Reuse/recycling.
2. Waste destruction (or conversion).
3. Media transfer.
4. Waste disposal.

Media transfer and disposal options may simply move the contamination to another location where it will have to be cleaned up again. Whereas reuse, recycling, and destruction technologies or processes offer more long-term or permanent solutions.

Monitored natural attenuation or passive bioremediation may provide cost-effective containment at some sites. In some instances where contamination exceeds remedial goals, but no immediate threats or impacts are identified, it may be acceptable to allow contamination to remain in place without active remediation. Monitored natural dilution, attenuation, and degradation processes would thus be allowed to slowly reduce concentration levels. However, this approach may require site-specific exposure and risk assessment, to determine threats and impacts to public health and the environment (Small, 1993).

3.4.2. Remedial Goals and Technology/Process Selection for Area 43 MWR Gas Station

Remedial goals have not currently been clearly established for the site. However, we can match some possible remedial technologies with some possible remedial goals in the following hypothetical examples:

Example (1)

Remedial Goal: Reduce concentrations at all points in the plume to a low value in a short period of time.

Potential Remedial alternative: Excavation of soil below the groundwater in the core of the plume and groundwater extraction with above ground treatment for soil and groundwater.

Monitored natural attenuation at the margins of the plume. Not only would this approach be extremely expensive, but excavation activities would almost certainly exert a detrimental effect on the Las Flores Creek ecology.

Example (2)

Remedial Goal: Reduce concentrations at all points in the plume to a low value in a longer period of time.

Potential Remedial Alternative (1): Enhanced and or engineered solutions to accelerate biodegradation in the core of the plume and groundwater extraction with above ground treatment for groundwater. Monitored natural attenuation at the margins of the plume. This approach would potentially reduce the concentrations of FHCs entering the Las Flores Creek, if such a processes is actually occurring. However, the installation and operation of an active pump-and-treat is expensive (and potentially could impact the Las Flores Creek ecosystem), thus an associated benefit must be demonstrated to justify such a course of action. Clearly, such a benefit would be defined by the reduction of FHC concentrations in the surface water of the creek. However, to date, FHCs have not been detected in the Las Flores Creek in the vicinity of the site. If FHC concentrations continue to remain below applicable detection limits in the surface water, then there is no real basis for a pump-and-treat system.

Potential Remedial Alternative (2): Source control solutions, working on concert with natural attenuation processes, to deplete the plume over time. For the Area 43 MWR Gas Station site, air sparging may offer a reasonably inexpensive alternative. This may require the installation of a new well or wells in the vicinity of B-9 and B-11, where the highest soil FHC concentrations have been detected near the water table.

Example (3)

Remedial Goal: Non-migration or containment of the plume, no demonstrable ecological or surface water impacts.

Potential Remedial Alternative: Passive bioremediation and monitored natural attenuation for the entire plume. Contingency plan for more active remediation should the plume be shown to measurably impact surface waters of the creek. However, a small-scale monitoring program could provide evidence that significant perturbations to the ecosystem as a result of the fuel hydrocarbon groundwater plume are not occurring.

4. Summary and Recommendations

Sources. Two 10,000-gallon gasoline storage tanks and one 550-gallon waste oil storage tank were removed from the Area 43 MWR Gas Station in 1993; associated piping was also repaired. Free product has not been observed in site groundwater monitoring wells and analyses of soil samples indicate that the remaining FHC concentrations are highly localized.

Pathways. Exposure pathways include groundwater and air (vapor). A potential groundwater exposure pathway clearly does exist with respect to the nearby Las Flores Creek, which is only some 100 feet downgradient of the source area. The vapor exposure pathway is limited as a result of the distance to nearby offsite buildings

Receptors. The primary at-risk receptor has been identified as the ecosystem supporting Least Bell's vireo population associated with the Las Flores Creek, which runs adjacent to the site. The nearest human risk receptors with respect to groundwater are water-supply wells located some four miles downgradient. These wells are not considered threatened by the release. Institutional controls should be in place to prevent the installation of new water-supply wells in the immediate vicinity of the FHC/MTBE plume. Risk receptors potentially exposed to hydrocarbon vapors would include occupants of residential barracks across Las Pulgas Road and

onsite buildings. Vapor exposure to onsite workers from the subsurface FHC release is not expected to be significant in comparison to exposure associated with daily activities at gasoline service stations in general.

In summary, three major risk management considerations are recognized:

1. FHC and MTBE impact to the Las Flores Creek may be occurring, although preliminary surface water sampling and analysis has failed to detect direct evidence of this. It is also possible that the FHC-impacted aquifer passes underneath the creek bed and thus does not pose as immediate a threat to the creek as direct discharge from the effluent aquifer.
2. Natural attenuation processes are indeed active at the site. Statistical evidence exists which suggests that passive bioremediation of dissolved FHCs is occurring within the aquifer. However, it is unlikely that the rate of passive bioremediation is sufficiently rapid to prevent impact to the creek, should the aquifer discharge directly into the creek. FHCs and/or MTBE which might be introduced into the creek will be attenuated through dilution in the creek waters as well as by volatilization into the atmosphere (particularly with respect to the more volatile FHC components such as BTEX).
3. Human risk receptors are not likely to be threatened. Given the potential discharge from the aquifer into the Las Flores Creek, ecological risk receptors could be threatened. However, it is probably not feasible to directly characterize or measure the extent of such a threat. Data are generally not available pertaining to FHC or MTBE concentration thresholds which could adversely impact the stream ecosystem. Given the probable low levels of FHCs or MTBE present in the system, detecting FHCs or MTBE in the surface water or in the tissues of local flora and fauna would be problematic. Furthermore, with a limited data set, identifying statistically significant indications of ecosystem damage which could be directly ascribed to FHC or MTBE contamination would also be extremely difficult. Finally, even if an FHC or MTBE footprint were somehow to be identified in the creek ecosystem, it is not a straightforward issue to link such an impact with subsurface releases when surface run-off from the asphalt cover to the service station could also play a role.

Thus, while a theoretical threat to the Las Flores Creek ecosystem in the vicinity of the Area 43 MWR Gas Station exists with regard to the FHCs and/or MTBE, the manifestations of such a contamination problem are not likely to be noticed or even measured.

However, a small-scale monitoring program could provide evidence that significant perturbations to the ecosystem as a result of the fuel hydrocarbon groundwater plume are not occurring. One way to define ecological value would be to relate it to the utility of the habitat for Least Bell's vireo populations. Ecological value would then be monitored through direct monitoring of vireo population abundance, or monitoring habitat components which make the habitat attractive to vireo populations (abundance of typical food sources, appropriate vegetation for suitable nesting sites, etc.). Data could be compared to a matched reference site along the creek where contaminant impacts would not be expected.

It is likely that some kind of monitoring program for Least Bell's vireo populations at Camp Pendleton may already exist. A Memorandum of Understanding (MOU) between the U.S. Fish and Wildlife Service and the Marine Corps was signed in 1989 for vireos within proposed critical habitat on Camp Pendleton. This MOU resulted in actions at Camp Pendleton to increase vireo abundance. Any monitoring program conducted as a result of this MOU could be potentially modified to monitor habitat value of Las Flores creek.

Thus, if plume containment is the remedial goal, it is our opinion that engineered remedial action such as groundwater pump-and-treat or additional source removal is unwarranted because there are no immediate demonstrable benefits of such actions. Under such conditions, the plume will slowly self-remediate over time as the source is exhausted. If the remedial goal involves accelerated plume diminishment, air-sparging as a means of source control, as opposed to active

pump-and-treat, may offer some measurable benefit. Regardless of the remedial goal, we do recommend at a minimum (1) continued monitoring of FHCs and MTBE at the site, particularly in MW-04, on at least an annual basis to assure that the FHC influx is stable or declining with time, (2) continued monitoring of MW-01A and/or MW-05B to assure that downward vertical migration of FHCs or additional MTBE does not occur, and (3) at least one additional round of surface water sampling in the Las Flores Creek immediately downstream of the service station to confirm the non-detections of FHCs and MTBE. We do not recommend extensive, invasive sampling in the creek area, as equipment and personnel would be likely to inflict damage to the ecosystem which could easily surpass that conceivably created by any FHCs present in soil or water.

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Figures

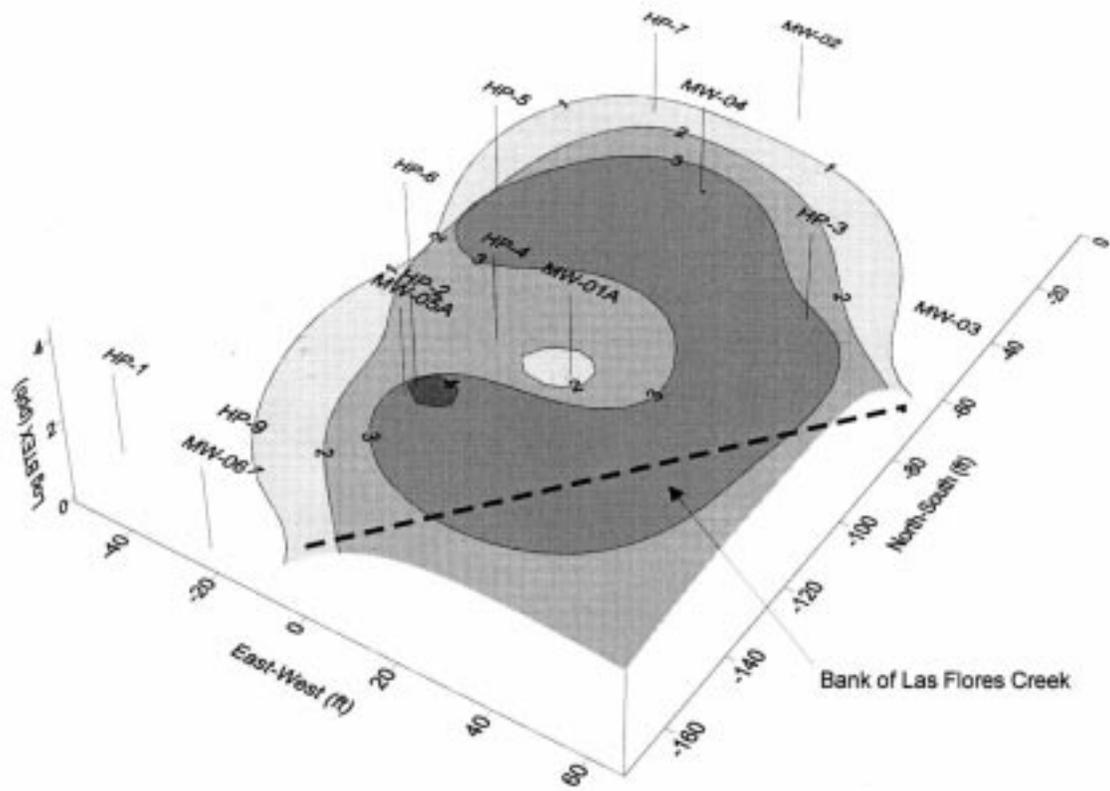


Figure 1. Interpolated concentrations of BTEX ($\log \mu\text{g/L}$) in Area 43 MWR Gas Station wells and cone penetrometer ground water samples (March-April 1997).

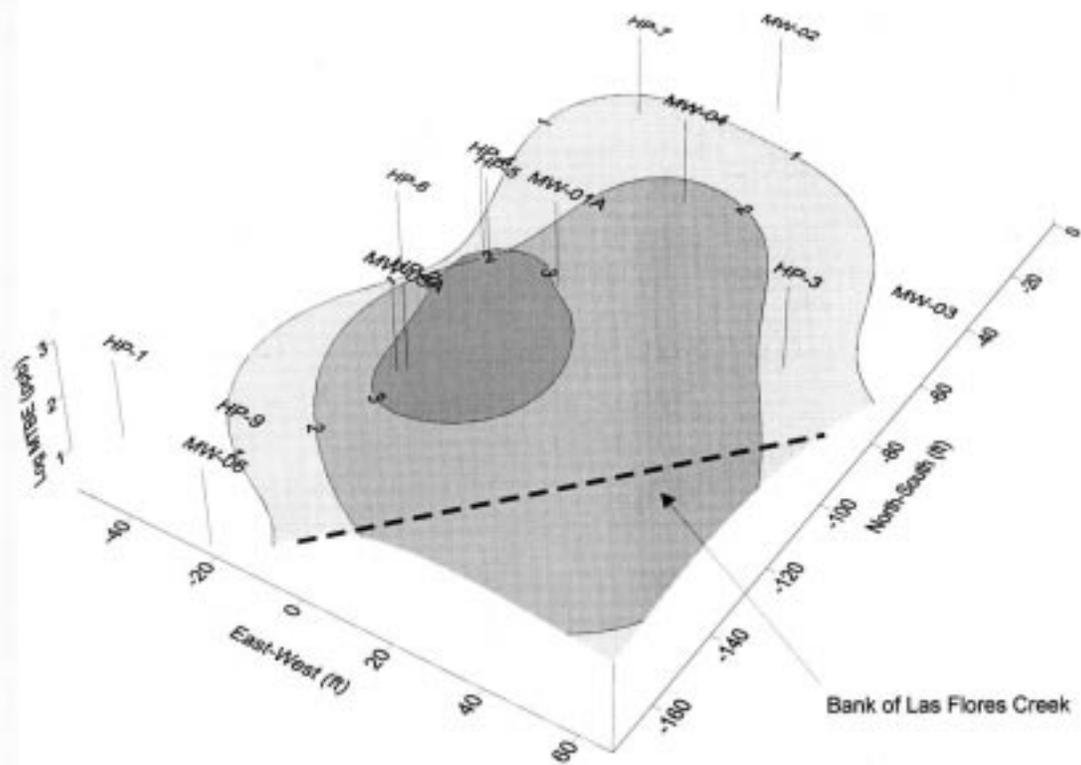


Figure 2. Interpolated concentrations of MTBE ($\log \mu\text{g/L}$) in Area 43 MWR Gas Station wells and cone penetrometer groundwater samples (March-April 1997).

Appendix A

Site Assessment Evaluation Letter



Lawrence Livermore National Laboratory

SITE ASSESSMENT REVIEW TO APPLY RISK BASED CORRECTIVE ACTION AT SITE 43 AREA GAS STATION CAMP PENDLETON MARINE CORPS BASE, CALIFORNIA

The Department of Defense California Petroleum Hydrocarbon Cleanup Demonstration Program Expert Committee (EC) has reviewed the methods and findings of the site investigations conducted at the Site 43 Area Gas Station at the Marine Corps Base (MCB) Camp Pendleton with regard to releases of gasoline to subsurface soils and groundwater. These investigations have been conducted by OHM Remediation Services Corporation and others. Included is our evaluation of the adequacy of the site conceptual model and risk characterization as a credible basis for applying risk-based corrective action (RBCA), emphasizing natural attenuation as a means of remediation, to achieve site closure.

This letter represents the first of two deliverable documents to be provided as part of our overall assessment. It is intended solely as a brief review of the existing data and risk characterization models; recommendations regarding additional data needed to complete the site model review are provided. Specifically, the review included:

- An assessment of site characterization and the contaminant distribution model, based upon conformance with standard environmental investigation practices and sound scientific judgment;
- A preliminary assessment of bioattenuation signatures, based upon presentation of multiple lines of evidence such as natural geochemical indicators and changes in plume composition over time;
- An assessment of risk characterization, based upon our judgment as to how significant uncertainties in risks posed to potential receptors have been characterized.

Detailed analyses of risk management key assumptions, an assessment of site-specific natural attenuation, and recommendations concerning risk-management strategies will be provided in a follow-up report as a separate deliverable item.

SITE CONCEPTUAL MODEL

Site History

The Site 43 Area Morale, Welfare, and Recreation (MWR) Gas Station is located in the Las Flores groundwater basin at the MCB. The Gas Station was constructed in 1958 and is currently operational. Two previous 10,000-gallon gasoline underground storage tanks (USTs) and one 550-gallon waste oil UST were removed from the site in October 1993. Fuel hydrocarbon compounds (FHCs) were detected in soil and groundwater associated with the site during an initial site assessment in 1994. The release history and release volume are not well known. Subsequent investigation activities, including drilling soil borings and installing groundwater monitoring wells, have been conducted in an effort to delineate the extent of contamination. No active remediation system is currently installed at the site. Groundwater quality data are being collected to support a possible remediation-by-

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natural-attenuation alternative, as suggested by the San Diego Regional Water Quality Control Board (SDRWQCB) in a letter to the MCB dated June 19, 1996.

Hydrogeologic Setting

The Site 43 Area Gas Station is located on approximately 15 feet of fill overlying the native sediments. The underlying native sediments are unconsolidated alluvial materials (interbedded sands, silts, and clays) of Quaternary age. An east-west trending geologic cross section made available to the EC suggests considerable hydrostratigraphic complexity; the degree of interconnection between permeable strata, and between monitoring points, is not immediately clear upon inspection. The results of an aquifer test previously conducted at the site would assist in clarifying the hydrostratigraphic model.

Average depth to groundwater at the site is approximately 15 feet, with observed seasonal fluctuations in groundwater elevation on the order of two feet. The aquifer is presumed to be in an unconfined condition; the relationship between the shallow FHC-impacted strata and deeper water-bearing zones has not been defined. The asphalt cover over much of the site is likely to preclude significant vertical recharge from infiltration. Groundwater flow direction is to the southeast. The average groundwater gradient across the site is approximately 0.032 ft/ft, which is considered to be quite high. However, hydraulic conductivity measurements obtained from the pumping test conducted in site wells were not available for the EC's review, so the actual groundwater flow velocity is currently unspecified.

The site lies approximately 100 feet to the north of the Las Flores Creek. Given the depth to groundwater at the site and the apparent elevation of the creek relative to the gas station, it is possible that the creek acts as an effluent stream (i.e., gaining water from subsurface discharge), although direct evidence of this has not been made available to the EC. A visual inspection of the embankment to the south and west of the gas station indicates no sign of springs or other surface discharge of groundwater.

Distribution of Contaminants

The current extent of FHC soil and groundwater contamination has been delineated by 13 soil borings and four groundwater monitoring wells. Soil contamination (TPH as gasoline, BTEX constituents) has been observed in at least five borings, with concentrations of TPH-G ranging up to 5,300 mg/Kg (at a depth of 8 ft in B-2, as well as at 15 ft in B-9 - above water table). While much of the soil contamination appears to be associated with the former tank locations, the FHC detections in B-1 and B-2 near the pump island location suggest that releases occurred from the piping system as well. The EC understands that the piping system was replaced during tank removal activities, but the extent of remaining soil contamination in association with the pump island is not well known.

It is the EC's understanding that free product has not been observed in site monitoring wells. The increasing soil concentrations of TPH-G and BTEX components with depth in B-11, with the highest concentrations immediately overlying the water table at 15 feet, suggest that a free product layer on the water table may have existed at one time near the tank locations. Synthetic precipitation leaching procedure (SPLP) tests have been conducted on site sediment samples in an attempt to quantify the potential for residual entrapped hydrocarbons in the vadose zone to impact groundwater.

FHCs have been detected in groundwater in MW-01 and MW-04 during 1995–1996 sampling events. MW-04 lies immediately downgradient of the former tank location, while

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MW-01 lies an additional 35 feet downgradient (toward the Las Flores Creek). The highest historical benzene concentration measured was approximately 3 mg/L in MW-04 in September, 1995. FHC concentrations have generally declined in MW-01 and MW-04 in subsequent sampling rounds since September 1995, although concentrations appeared to increase somewhat in November 1996, the most recent monitoring data available.

The decline in FHC concentrations between MW-01 and MW-04 provides some evidence that the extent of the groundwater plume is limited at the site. Fuel hydrocarbons have generally not been detected in the cross-gradient well, MW-03, or in the upgradient well, MW-02, with the exception of a December 1993 sampling event which revealed 41 mg/L and 400 mg/L TPH-G, respectively, in these wells. These previous detections, particularly in the upgradient well, are not easily explained in the context of the present understanding of the site. It should be recognized that the well density at the site, given the apparently complex nature of the subsurface hydrostratigraphy and the high groundwater gradient, may fail to reveal preferential transport pathways or undiscovered sources which may contribute to FHC impact to groundwater.

The fuel-oxygenate methyl tertiary butyl ether (MTBE) has been detected in site groundwater in association with the FHCs (MW-01 and MW-04). The highest concentration detected to date has been approximately 1 mg/L in MW-04 in October 1996.

Natural Attenuation Indicators

Inorganic geochemical indicator parameters of biodegradation (dissolved oxygen, nitrate, sulfate, ferrous iron, sulfide, redox potential) have been measured in all four monitoring wells in November 1996. There is some indication of anaerobic activity in MW-01, MW-03, and MW-04 in comparison to MW-02 (e.g., depleted nitrate, presence of ferrous iron and sulfide and reduced redox potential in MW-03 and MW-04). However, given the small size of the sample set, the overall statistical significance of these observations must be carefully evaluated.

IDENTIFICATION OF RISK RECEPTORS

Human Risk Receptors

The gas station is currently active, with barracks, administration buildings, and warehouses with 1000 feet. Local population density depends upon the nature of military deployments. Thus, there are theoretical vapor receptors in the area, although the apparent absence of free product and the asphalt covering greatly diminishes the risk of exposure. No drinking water wells currently exist within four miles of the site

Ecological Risk Receptors

The Las Flores Creek, immediately downgradient of the release location, is home to the endangered Least Bell's Vireo, and thus constitutes a potential ecological risk receptor, particularly if habitat is disrupted during characterization or remediation activities in the creek bed. The potential for FHCs to impact the stream via discharging groundwater warrants evaluation and will be addressed by the EC in the forthcoming Risk Management Report.

SUMMARY

It appears likely that the FHCs detected in soil and shallow groundwater at the Site 43 Area Gas Station are relatively limited in terms of their spatial extent. The extent of the FHC plume may be limited by groundwater discharge to Las Flores Creek. Free product is not evident and groundwater contamination, as indicated by the four monitoring wells installed on the site, appears to be largely limited to the vicinity of the former USTs. As indicated by local regulators, the site may be a good candidate for the application of passive bioremediation. Nevertheless, for passive bioremediation to be considered as a remediation alternative, the conceptual model of the site, and knowledge of the extent of contamination, should be improved. Specifically, the EC requests the following information be made available to enable completion of our site assessment report:

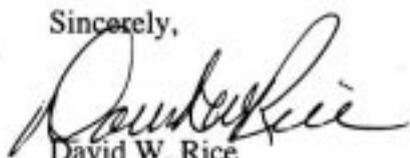
- The pilot test report, mentioned during the EC's site visit on January 28, 1997, describing aquifer tests and vapor extraction tests conducted by IT Corporation;
- The tank removal report.

In addition, we recommend the following actions be taken to improve understanding of the distribution of FHCs and their behavior in the subsurface:

- Continued quarterly groundwater sampling of all four wells through July, 1997, as planned by OHM Remediation Services Corporation. Analyses should include not only TPH-G, BTEX, and MTBE, but also the inorganic geochemical bioattenuation indicators (as measured in the November, 1996 sampling round);
- Refinement of site shallow aquifer conceptual model by integrating subsurface lithology with the results of previous aquifer tests;
- Additional subsurface soil and groundwater sampling, using Hydropunch or similar techniques, in the area south of B-1, MW-01, and MW-04, to better characterize the extent of soil contamination associated with the pump islands and to assist in reducing the uncertainty in the southern extent of the FHC groundwater plume.

We look forward to preparing our site assessment report following receipt of this information.

Sincerely,

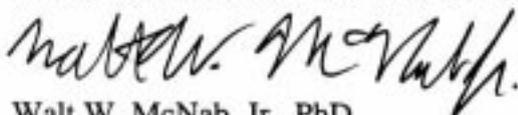


David W. Rice

Program Director

Department Of Defense Petroleum Hydrocarbon Cleanup Demonstration Program

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Walt W. McNab, Jr., PhD

Environmental Scientist

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Expert Committee Lead for MCB Camp Pendleton Site 43 Area Gas Station

DWR/WWM:cak

Appendix B

Assessing Ecological Impacts

Appendix B

Assessing Ecological Impacts

Determining the potential for ecological damage as a consequence of chemical releases into the environment is recognized as a critical component of hazard assessment (Suter and Loar, 1992; Carlsen 1996). Indeed, several federal statutes (such as CERCLA, RCRA, and FIFRA), require the identification and mitigation of ecological impacts associated with chemical releases into the environment. As a result, a variety of methods are available to estimate the ecological hazard from chemical releases. These methods range from the qualitative to quantitative (Solomon, 1996; USEPA, 1992; Warren-Hicks et al., 1989). Most of these methods share some basic elements. Typically, an evaluation of the potential pathways in which ecological receptors can be exposed to the chemical is conducted. The groups of exposed organisms are identified and the probable level of exposure determined. Finally, the ecological significance (if any) of this exposure is identified. While this last step is the most crucial, it is often the most difficult. While demonstrating exposure of an ecological receptor to a chemical is clearly necessary, it is not sufficient to determine that an ecologically meaningful impact has occurred.

The exposure analysis will likely result in the identification of numerous species which could potentially be exposed to chemicals released into the environment. It is often necessary to group the biota into major ecological functional groups to simplify the initial exposure pathway analysis. Once the initial exposure pathway analysis is complete, specific groups of organisms may be selected for in-depth hazard assessment. Organisms selected for the detailed analysis are often considered "sentinel organisms" (Suter et al., 1987; Grizzle et al., 1988; Rice et al., 1994). When evaluating ecological exposure, it is necessary to identify or consider (1) the organisms that are actually or potentially exposed and the exposure level, (2) the significant routes of exposure, (3) the spatial and temporal scales of exposure, and 4) the geophysical, physical and chemical properties that could affect exposure.

To determine the ecological significance of exposure to a chemical, it is necessary to select ecological endpoints to be examined. Endpoints are characteristics of an ecological component (such as fish mortality) that may be affected by exposure to a stressor (Suter, 1990; USEPA, 1992). It is useful to distinguish between two types of endpoints, assessment endpoints and measurement endpoints. Assessment endpoints are explicit expressions of the actual environmental values that are to be protected (USEPA, 1992; Warren-Hicks et al., 1989). Measurement endpoints are the measurable responses to a stressor that are related to the valued characteristics chosen as the assessment endpoint (Suter, 1990). In some cases, measurement endpoints and assessment endpoints are equivalent.

Although there are a number of ways to specifically define ecological assessment endpoints, in general they should (1) be relevant to society, (2) have biological or ecological relevance, (3) have an unambiguous operational definition, (4) be measurable or predictable, (5) be susceptible to hazard, and (6) be logically related to the policy or remedial decisions. In the context of evaluating the ecological impacts of petroleum hydrocarbon exposure, assessment endpoints

should be environmental characteristics that if significantly affected would indicate the need for some type of action.

If endangered species are not involved, plants and animals are typically not valued biologically as individuals, and therefore the assessment endpoints are usually related to entire populations or communities (Warren-Hicks et al., 1989; Moriarty, 1983). An example of a population-based assessment endpoint would be "change in the abundance of aquatic or amphibian populations". However, due to their rarity, individual members of endangered species are considered essential to the survival of the species. In this case assessment endpoints related to individuals are appropriate.

As mentioned above, measurement endpoints are a quantitative expression of an observed or measured effect of a stressor that is related to the valued characteristic chosen as the assessment endpoint. Measurement endpoints should have specific characteristics, depending on the problem at hand. Most importantly, measurement endpoints should (1) correspond to or be predictive of an assessment endpoint, (2) be readily measured, (3) be appropriate for the scale of the problem, (4) be appropriate to the exposure pathway, (5) be appropriate to temporal dynamics, (6) have low natural variability, and (7) be diagnostic of the contaminant of interest.

Continuing with the example given for an assessment endpoint, corresponding measurement endpoints might include "reduced number of fish eggs hatching." This measurement endpoint clearly relates to the assessment endpoint. However, such measurement endpoints can require maintaining large lab populations for a significant length of time or conducting lengthy field studies. Recent research has focused on identifying biochemical changes which are precursors to reduced reproductive success. Examples include binding affinity to estrogen receptors and induction of the mixed-function oxidase (MFO) enzyme system. However, care must be taken when using such biochemical measurement endpoints to show that they directly tie to the assessment endpoint.

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Appendix C

Evaluation of Hydrocarbon Passive Bioremediation in Groundwater

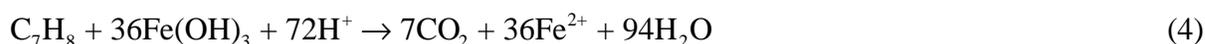
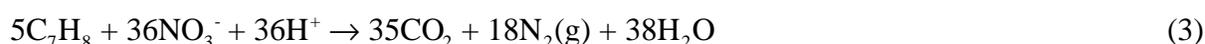
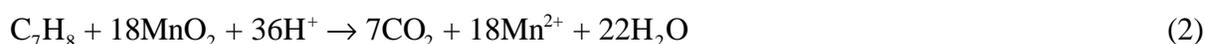
Appendix C

Evaluation of Hydrocarbon Passive Bioremediation in Groundwater

Spatial distribution patterns in certain geochemical biodegradation indicators correlate reasonably well with the distribution of total BTEX (e.g., Fig. C-1). To provide more quantitative analyses, statistical methods were also utilized to identify secondary evidence of passive bioremediation.

C-1. Background

Identifying evidence of FHC biodegradation from field data is a key element in formulating risk management strategies that incorporate natural attenuation at groundwater contamination sites. Primary evidence of biodegradation (i.e., observed decline in total contaminant mass over time) is often difficult to extract from monitoring data because of sparse sampling networks and short sampling histories. Therefore, secondary lines of evidence must often be pursued. Typically, secondary evidence consists of an assessment of changes in groundwater geochemistry associated with the FHC plume which may reflect the oxidation of FHCs by microorganisms (e.g., Vroblesky and Chapelle, 1994; Borden et al., 1995). For example, idealized mineralization reactions of toluene, a common soluble and degradable FHC constituent, to yield carbon dioxide could include:



Laboratory studies have confirmed FHC biodegradation reactions by specific electron acceptors (e.g., Lovley et al., 1989; Beller et al., 1992; Lovley et al., 1995; Vroblesky et al., 1996). Thus, solution constituents which may serve as biodegradation indicators include electron acceptors (dissolved oxygen, nitrate, sulfate), reduced by-products of FHC oxidation reactions (ferrous iron,

manganese, methane), solution redox potential or E_h , and indicators of mineralization (bicarbonate alkalinity, pH via dissociation of carbonic acid). Sulfide, also a reduced by-product of FHC biodegradation, is often not measurable because of the low solubility of sulfide-bearing minerals under typical E_h -pH conditions.

Each of these indicator parameters is subject to a certain degree of variability in background concentrations. Given the sparse monitoring well network often associated with FHC release sites, it may often be difficult to discern patterns in spatial distributions of geochemical indicators which offer unequivocal proof of biodegradation. In regard to this problem, two particular issues warrant attention: (1) Which geochemical indicators are the most reliable, and (2) Which statistical methods are available that offer the most powerful means for extracting biodegradation signatures from field data? To address these issues, geochemical indicator data were analyzed using a variety of statistical methods to identify trends in the data with respect to measured FHC concentrations. Statistical tests included correlation analyses which quantify the relationship between geochemical indicators (dissolved oxygen, nitrate, sulfate, iron, methane, alkalinity, E_h) and benzene, toluene, ethylbenzene, and xylenes (BTEX). Methods for testing for significant differences between two data populations (e.g., geochemical indicators from BTEX-contaminated and noncontaminated monitoring wells) were also explored.

C-1.1. Correlation Analyses

Correlation analyses involve quantifying the degree to which geochemical indicator parameter values reflect total BTEX concentrations in individual water samples (BTEX constituents being among the most soluble and most easily biodegraded among FHCs). Correlation coefficients near +1.0 or -1.0 reflect strong positive or negative relationships, respectively, implying that biodegradation reactions dominate the observed variance in the indicator being tested. Correlation coefficients near 0.0 indicate no significant relationship and that biodegradation processes exert little or no measurable impact on observed variance, suggesting that other explanations such as background variability are more significant.

Two different approaches were used to quantify the correlation coefficient, R . The most familiar form is the linear correlation coefficient given by the Pearson relationship,

$$R = \frac{\sum_{i=1}^N (X_i - X_m)(Y_i - Y_m)}{\sqrt{\sum_{i=1}^N (X_i - X_m)^2} \sqrt{\sum_{i=1}^N (Y_i - Y_m)^2}} \quad (7)$$

where N is the number of samples, X_i and Y_i the values of the independent and dependent variables, respectively (i.e., total BTEX and the geochemical indicator value in sample i), and X_m and Y_m the respective mean values of the sample sets.

An alternative approach for quantifying the correlation coefficient is the nonparametric Spearman relationship (Langley, 1970; Miller and Freund, 1977),

$$R = 1 - \frac{6 \sum_{i=1}^N d_i^2}{N(N^2 - 1)} \quad (8)$$

where d_i is the difference in ranks between two observations. If two or more data values are tied, they are each assigned the mean rank jointly occupied. The primary advantage of rank-based approach is that strong nonlinearities in the correlation relationship will not unduly skew the resulting estimated correlation coefficient. This is an important factor with regard to BTEX concentrations, which tend to be lognormally distributed rather than normally distributed.

C-1.2. Hypotheses Testing Concerning Two Population Means

A second approach for assessing the relationship between BTEX and potential passive bioremediation indicators is to compare indicator values from both BTEX-contaminated and uncontaminated wells to test if the two data sets are distinct. The student's t-test is one approach which may be used for such a comparison (Miller and Freund, 1977). The general student's t-test evaluates the hypothesis that two sample sets have the same mean, assuming that they both are characterized by the same variance. The test statistic calculated by the general test is:

$$t = \frac{X_{1,m} - X_{2,m}}{\sqrt{\frac{\sum_{i=1}^{N_1} (X_i - X_{1,m})^2 + \sum_{i=1}^{N_2} (X_i - X_{2,m})^2}{N_1 + N_2 - 2}}} \quad (9)$$

where N_1 and N_2 are the respective number of observations in each sample set, X_1 and X_2 the values of individual observations (i.e., geochemical indicator values for BTEX-contaminated and uncontaminated wells, respectively) and $X_{1,m}$ and $X_{2,m}$ the respective mean values of the sample sets. The unpaired student's t-test assumes that the two samples do not have the same variance. In this case, the test statistic is calculated by:

$$t = \frac{X_{1,m} - X_{2,m}}{\left(\frac{\sum_{i=1}^{N_1} (X_{1,i} - X_{1,m})^2}{N_1(N_1 - 1)} + \frac{\sum_{i=1}^{N_2} (X_{2,i} - X_{2,m})^2}{N_2(N_2 - 1)} \right)^{1/2}} \quad (10)$$

The paired student's t-test assumes that much of the variance in both samples is due to effects that are point-by-point identical in the two samples. Pairs of observations are randomly assembled and tested from each sample set, extra unpaired observations from the larger set are discarded. The test statistic for the paired test is given by:

$$t = \frac{X_{1,m} - X_{2,m}}{\left(\frac{\sum_{i=1}^{N_1} (X_{1,i} - X_{1,m})^2}{N(N_1 - 1)} + \frac{\sum_{i=1}^{N_2} (X_{2,i} - X_{2,m})^2}{N(N_2 - 1)} - 2 \sum_{i=1}^N (X_{1,i} - X_{1,m})(X_{2,i} - X_{2,m}) \right)^{1/2}} \quad (11)$$

where N is the number of observation pairs.

For each method, the t-test statistic is calculated and compared with standard tables of critical test values. From these tables, the probability of the null hypothesis—the likelihood that both sample sets exhibit the same mean value—may be quantified. Nonparametric tests may also be employed. Rank-sum tests involve ranking observations in accordance with their magnitude, with tests performed on various combinations of ranks. The Mann-Whitney U-test statistic is given by,

$$U = N_1 N_2 + \frac{N_1(N_1 + 1)}{2} - R_1 \quad (12)$$

where N_1 and N_2 are the respective sample sizes and R_1 the sum of the ranks assigned to the values of the first sample (Miller and Freund, 1977). The U-test statistic may be compared with a standard table to assess probability of the null hypotheses of equal means.

C-2. Results

Total BTEX concentrations and geochemical biodegradation indicators in groundwater samples from eight monitoring wells and eight cone penetrometer tests in March–April 1997 were included in the analyses. Correlation coefficients are shown on Table C-1. Indicators are ranked in decreasing order of reliability by the Spearman test. Correlations estimated by the Pearson relationship were calculated using both linear and logarithmic scales for total BTEX concentration. Correlation between BTEX and chloride ion, which would not be expected, is also presented for comparison as a control.

Table C-1. R-values (correlation coefficients) between total BTEX and geochemical biodegradation indicators. Chloride is presented as a control.

Parameters	Pearson	Spearman
BTEX: E_h	-0.675	-0.943
BTEX: CH_4	0.360	0.723
BTEX:Alkalinity	0.650	0.718
BTEX:Fe(II)	0.554	0.698
BTEX:Dissolved O_2	-0.495	-0.459
BTEX: SO_4^{2-}	-0.423	-0.415
BTEX: NO_3^-	-0.135	-0.099
BTEX: Cl^-	-0.102	-0.033

The trends in each of the indicator parameters are all consistent with expected variations in association with FHC passive bioremediation, although some species, particularly nitrate, exhibit poor correlation. For example, concentrations of ferrous iron exhibit a positive correlation with total BTEX, suggesting that iron reduction and mobilization is occurring in groundwater at the site (Lovley et al., 1989), while the negative correlation between sulfate and BTEX suggests sulfate reduction. Correlation coefficients are highest for redox potential, ferrous iron, and methane. The low correlation coefficients which characterize oxygen, nitrate, and sulfate are probably indicative of variability in background concentrations. As expected, chloride shows essentially no correlation with total BTEX.

Null-hypothesis probabilities (i.e., the probability that the geochemical indicator observations from BTEX-contaminated and noncontaminated water samples are taken from the same sample population) are shown on Table C-2. Results are ranked in accordance with the Mann-Whitney U-test probabilities. Regardless of the test method used, the null hypothesis does not appear to be correct for most of the indicators (with the exceptions of nitrate and possibly sulfate). Thus, most of the geochemical indicators appear to reflect different probability distribution functions between BTEX-contaminated and noncontaminated samples. For comparison, chloride samples from both sample sets were also tested as a control. Results of each of the methods suggest that no significant difference exists between the chloride concentrations in contaminated and noncontaminated wells, which is consistent with expectation.

Table C-2. Probabilities of equal means between geochemical indicator parameters measured in BTEX-contaminated and noncontaminated water samples; low probabilities imply a high likelihood that the two sample sets are distinct. Chloride is presented as a control.

Parameter	General	Unpaired	Paired	Mann-Whitney
Fe(II)	5%	5%	12%	0%
E _h	0%	0%	0%	0%
Alkalinity	2%	3%	6%	4%
CH ₄	13%	10%	11%	8%
Dissolved O ₂	6%	9%	6%	18%
SO ₄ ²⁻	30%	26%	28%	32%
NO ₃ ⁻	98%	98%	97%	72%
Cl ⁻	80%	81%	73%	86%

In summary, both statistical approaches, correlation analyses and hypothesis testing concerning population means, suggest that FHC passive bioremediation is occurring to some degree in the subsurface at the site. Beyond this assessment, it is difficult to quantify a mean degradation rate. A comparison between geochemical indicator concentrations in BTEX-contaminated and noncontaminated wells would suggest that approximately one to two degradation half-lives transpire during groundwater residences times within the plume based on simple reaction stoichiometry. However, these estimates must be interpreted with great caution, since uncertainty due to spatial variability of biodegradation reactions, residual BTEX and other FHC sources, and

other geochemical mechanisms not directly related to the FHCs probably exert major influences on the groundwater chemistry.

It should be noted that the findings with regard to passive bioremediation pertain only to BTEX compounds and not to MTBE. To date, conclusive field evidence of MTBE biodegradation or abiotic transformation has not been identified.

References

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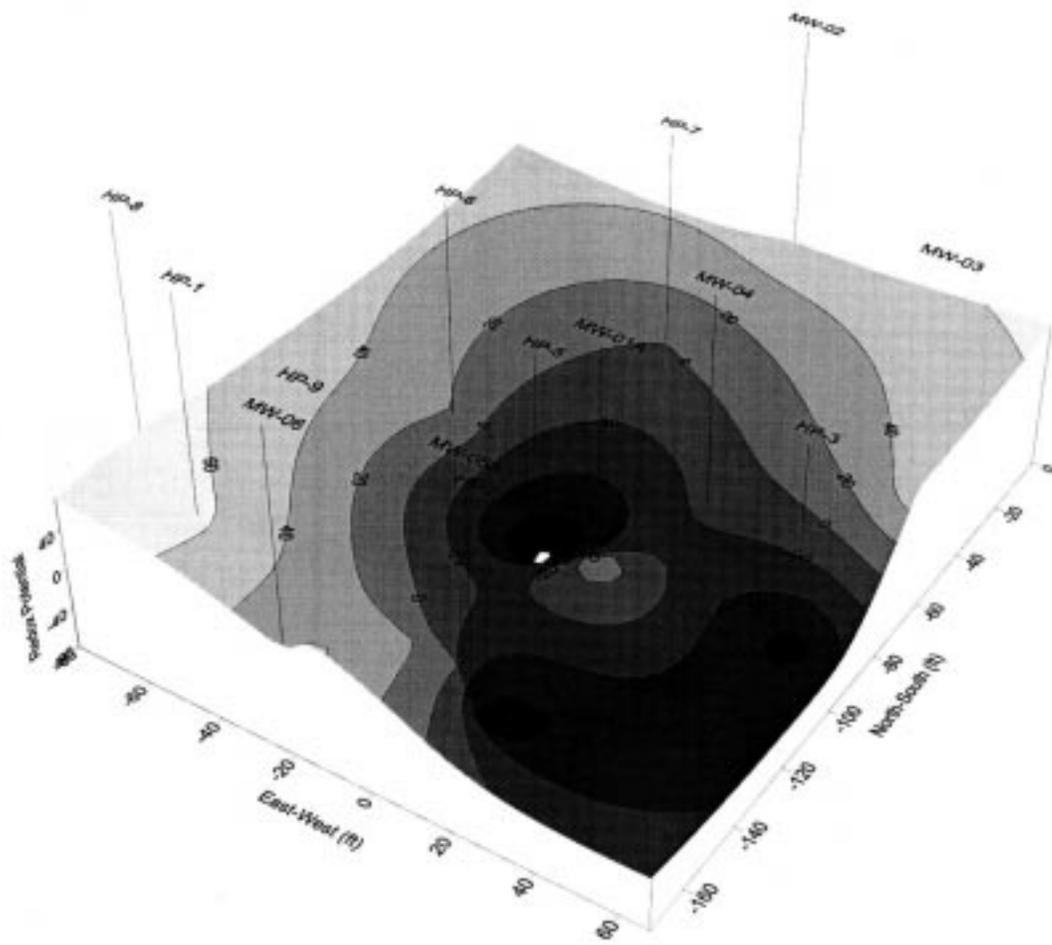


Figure C-1. Interpolated redox potential (mV) in Area 43 MWR Gas Station wells and cone penetrometer groundwater samples (March-April 1997).